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(58) Field of Search
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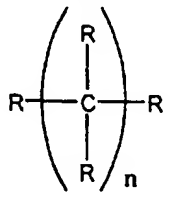
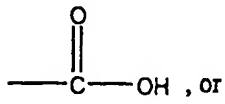
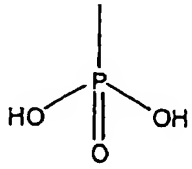
(54) Abstract Title
Set-retarding admixture for calcium sulfoaluminate cements

(57) A set-retarding admixture for calcium sulfoaluminate cements, comprises at least one phosphono alkyl carboxylic acid and/or salt thereof, and at least one carboxylic acid and/or salt thereof, the phosphono alkyl carboxylic acid having the structure



wherein R is independently selected from -H,  , or



and n is an integer from 3 to 6, with the proviso that at least one R is $PO(OH)_2$.

The phosphono alkyl carboxylic acid may be 2-phosphono - 1,2,4- butane tricarboxylic acid and the carboxylic acid may be tartaric acid.

The phosphono alkyl carboxylic acid may be the sole retarder present in a cementitious formulation comprising a calcium sulfoaluminate cement.

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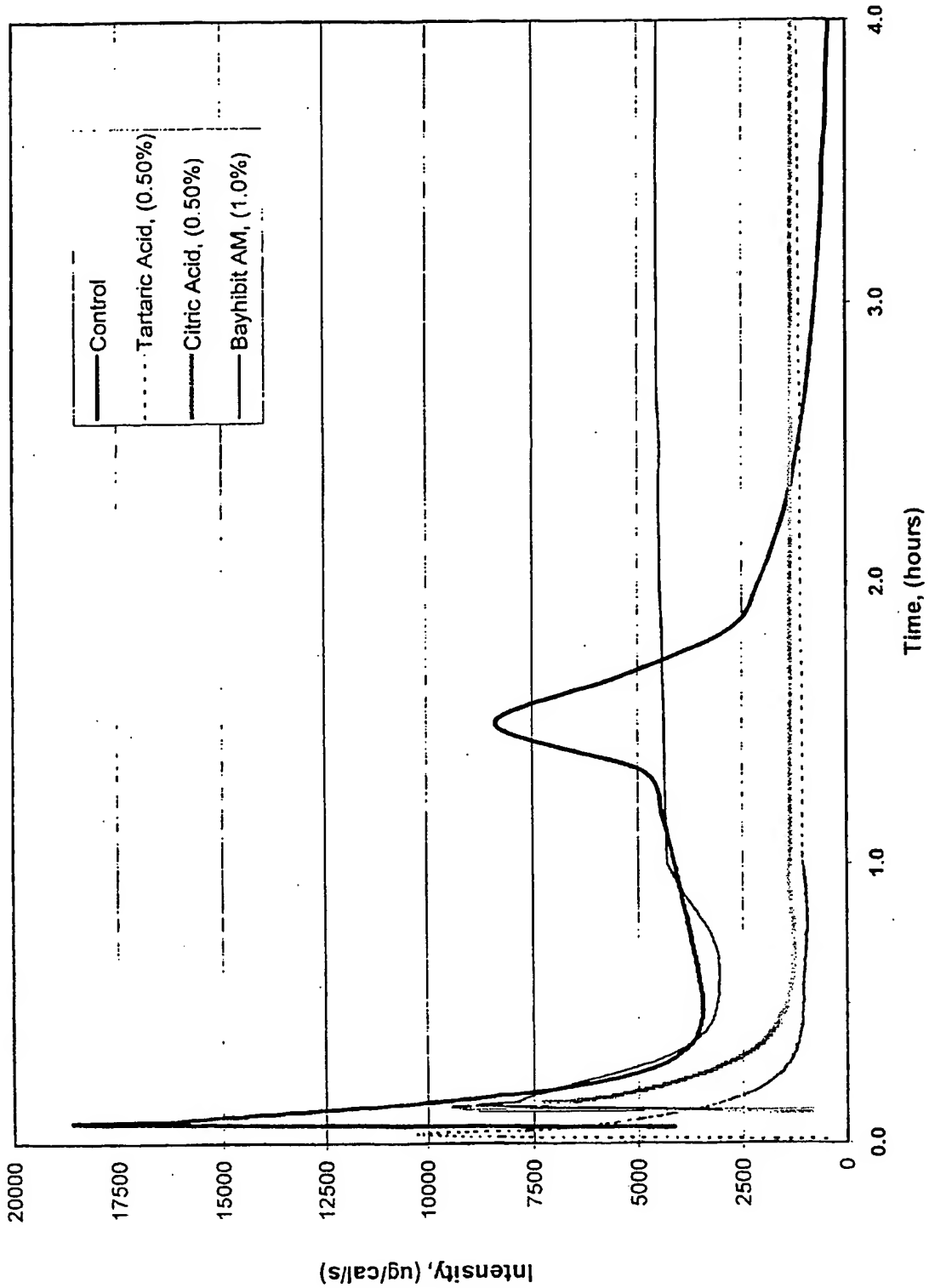
Figure 1. CSA Cement Hydration with Retarding



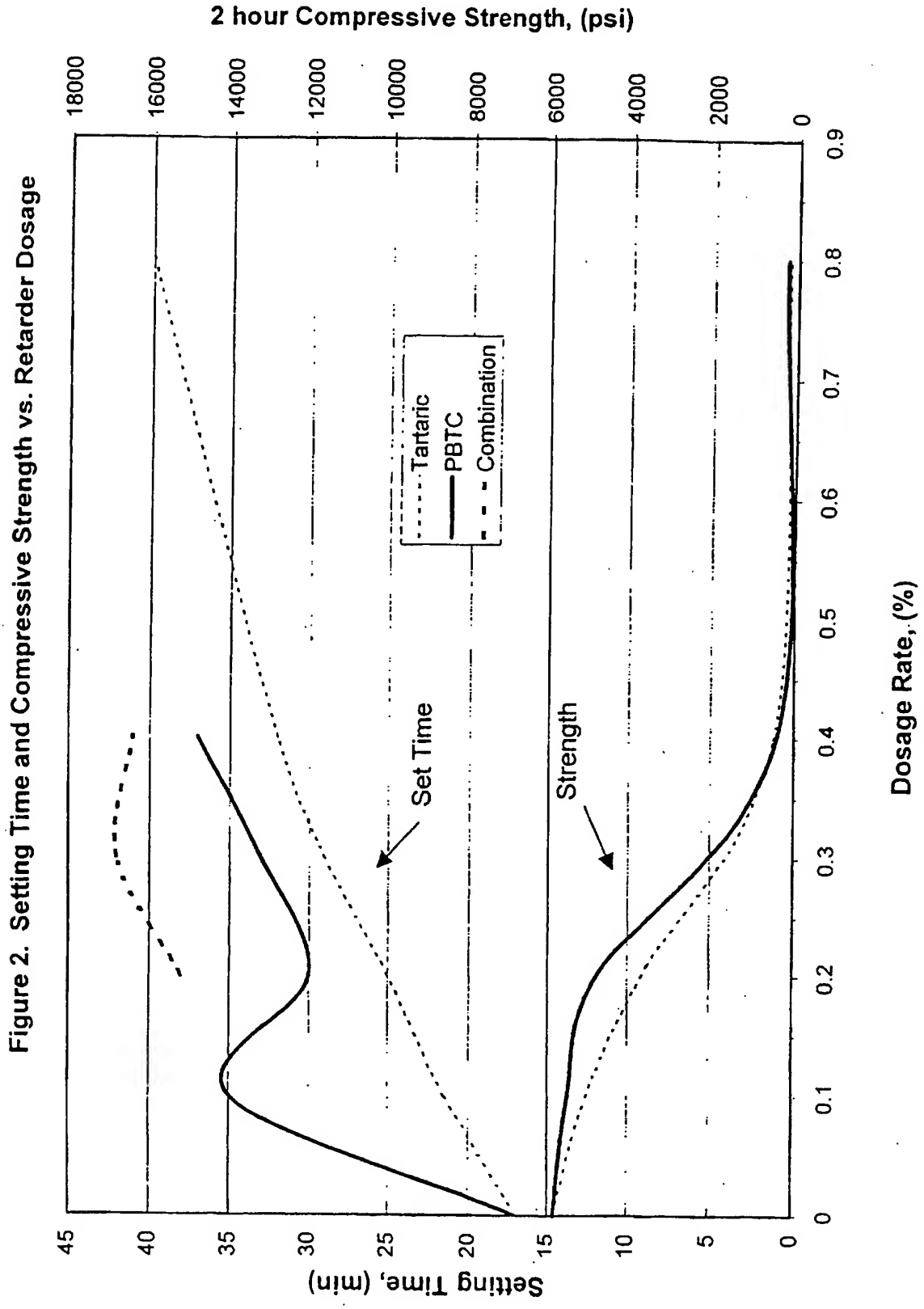


Figure 2. Setting Time and Compressive Strength vs. Retarder Dosage

RETARDER FOR CALCIUM SULFOALUMINATE CEMENTS

FIELD OF THE INVENTION

The present invention is directed to a retarder for calcium sulfoaluminate cements. More particularly, the present invention is directed to a retarder for calcium sulfoaluminate cements comprising phosphono alkyl carboxylic acid and/or its salts, either alone or in combination with a carboxylic acid and/or its salts.

BACKGROUND OF THE INVENTION

Calcium sulfoaluminate (CSA) cements generally comprise cements containing the components $4CaO \cdot 3Al_2O_3 \cdot SO_3$, $CaSO_4$, and CaO. When CSA cements are hydrated, ettringite is formed by the following reaction:

$$4CaO \cdot 3Al_2O_3 \cdot SO_3 + 8CaSO_4 + 6CaO + 93H_2O \rightarrow 3(CaO \cdot Al_2O_3 \cdot 3CaSO4 \cdot 31H_2O)$$

The formation of ettringite is very fast. This reaction provides for high early compressive strength of a cementitious formulation; however, this reaction causes the loss of workability of the cementitious formulation. To slow down the reaction and provide increased workability, retarders have been added to slow the hydration reaction in CSA cements. Typically, the retarders chelate the calcium and thus slow the hydration reaction.

While it has been known to use carboxylic acids, such as citric acid or tartaric acid, as retarders in calcium sulfoaluminate cements, these carboxylic acids require a large dose to be effective at retarding the reaction. At higher doses, not only is the set retarded, but the compressive strength of a resulting cement is also reduced. Increased workability is achieved at the cost of decreased compressive strength.

To overcome the problems with decreased compressive strength, carboxylic acids have been used in combination with other additives to seek to recapture some of the lost compressive strength. It has also been known to use phosphono butane tricarboxylic acids and phosphono aliphatic carboxylic acids as set retarders, but not in

connection with calcium sulfoaluminate cements.

What is needed in the industry is a set retarder for calcium sulfoaluminate cements that retards the set of the cement without a significant reduction in the compressive strength of a resulting cement.

It is therefore an object of the present invention to provide an admixture that retards the hydration of calcium sulfoaluminate cements without a significant reduction in the compressive strength of the cement.

It is another object of the present invention to provide a calcium sulfoaluminate cement formulation containing a retarder that retards the hydration of the calcium sulfoaluminate cement without a significant reduction in the compressive strength of the cement.

SUMMARY OF THE INVENTION

The present invention is directed to a set retarding admixture for calcium sulfoaluminate cements comprising a first component that is at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid, and a second component comprising at least one of a carboxylic acid and a salt of a carboxylic acid.

The present invention is also directed to a cementitious formulation comprising a calcium sulfoaluminate cement and a retarder, wherein the retarder comprises a component being at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid. Additionally, the retarder can comprise at least one of a carboxylic acid and a salt of a carboxylic acid.

The present invention is also directed to a method of retarding the set of a calcium sulfoaluminate cementitious formulation without substantially reducing achievable compressive strength, comprising providing in said cementitious formulation, a retarder comprising a component being at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid, and wherein the

calcium sulfoaluminate cementitious formulation comprises a calcium sulfoaluminate cement.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph comparing the retarding properties of selected retarders for calcium sulfoaluminate cements.

Figure 2 is a graph of setting time versus dosage of the retarder and a graph of the two hour compressive strength versus dosage of the retarder.

DETAILED DESCRIPTION OF THE INVENTION

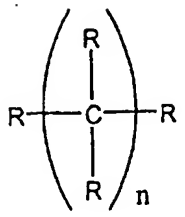
For simplification in writing, as used herein, the term acid/salt refers to the acid and/or the salt form of the chemical.

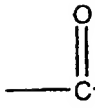
One embodiment of the present invention is directed to a set retarding admixture for calcium sulfoaluminate cements comprising a component that is at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid.

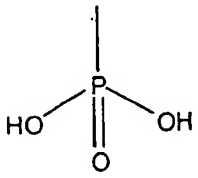
The salt of the phosphono alkyl carboxylic acid is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, ammonium, and mixtures thereof. The preferred salts are sodium and potassium.

The preferred phosphono alkyl carboxylic acid/salt is 2-phosphono-1,2,4-butane tricarboxylic acid (PBTC).

The phosphono alkyl carboxylic acid has the general structure shown below:

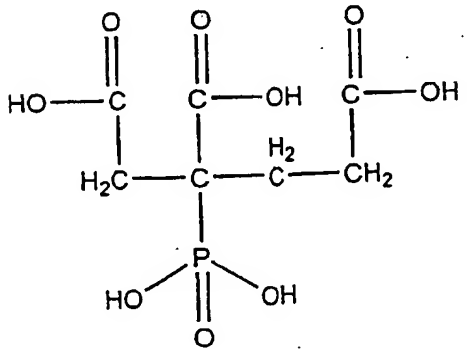


wherein R is independently selected from -H,  , or



and n is an integer from 3 to 6, with the proviso that at least one R is $PO(OH)_2$.

The preferred 2-phosphono-1,2,4-butane tricarboxylic acid is represented by the following structure:



The set retarding admixture further comprises a second component that is at least one of a carboxylic acid and a salt of a carboxylic acid. The carboxylic acids according to the invention generally have a 1 to 8 carbon atom backbone. The preferred carboxylic acids have 3 to 4 carbon atoms in the backbone. Suitable carboxylic acids according to the present invention include, but are not limited to, tartaric acid, citric acid, glutamic acid, glutaric acid, glycolic acid, formic acid, gluconic acid, and mixtures thereof. The preferred carboxylic acids are the hydroxy carboxylic acids.

The salts of the carboxylic acids according to the present invention include, but are not limited to, lithium, sodium, potassium, magnesium, and calcium salts of the previously referenced carboxylic acids. The preferred salts are sodium and potassium.

It has been found that the acid form of the phosphono alkyl carboxylic acid or the carboxylic acids is generally more effective at retarding the calcium sulfoaluminate cement than are the corresponding salts.

When the tartaric acid/salt is used in combination with the PBTC acid/salt, the effective ratio of the tartaric acid/salt to the PBTC acid/salt in the retarder according to the present invention ranges from greater than 0 to about 5 based on weight, and from greater than 0 to about 2.8 based on molar ratio. A preferred ratio of the carboxylic acid/salt to the PBTC acid/salt is about 2 to 1.

Another embodiment of the present invention is directed to a cementitious formulation comprising a calcium sulfoaluminate cement and a retarder, wherein the retarder comprises a component being at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid. The salt of phosphono alkyl carboxylic acid is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, ammonium, and mixtures thereof. The preferred salts are sodium and potassium.

The preferred phosphono alkyl carboxylic acid is 2-phosphono-1,2,4-butane tricarboxylic acid.

The retarder is present in the cementitious formulation in an amount from greater than 0% to about 1% based on the dry weight of the calcium sulfoaluminate cement. Preferably, the retarder is present in an amount of from about 0.2% to about 0.8% based on the dry weight of the calcium sulfoaluminate cement.

The retarder in the cementitious formulation of the present invention can further comprise a second component that is at least one of a carboxylic acid and a salt of a carboxylic acid. As stated above, the carboxylic acids generally have a 1 to 8 carbon

atom backbone,and preferred carboxylic acids have 3 to 4 carbon atoms in the backbone. Suitable carboxylic acids according to the present invention include, but are not limited to, tartaric acid, citric acid, glutamic acid, glutaric acid, glycolic acid, formic acid, gluconic acid, and mixtures thereof. The preferred carboxylic acids are hydroxy carboxylic acids.

The salts of the carboxylic acids according to the present invention include, but are not limited to, lithium, sodium, potassium, magnesium, and calcium salts of the previously-referenced carboxylic acids. The preferred salts are sodium and potassium.

The phosphono alkyl carboxylic acid/salt component of the retarder is present in the cementitious formulation in an amount from greater than 0% to about 0.4% based on the dry weight of the calcium sulfoaluminate cement. Preferably, the phosphono alkyl carboxylic acid/salt component is present in an amount from about 0.05% to about 0.3% based on the dry weight of the calcium sulfoaluminate cement.

The carboxylic acid/salt component is present in the cementitious formulation in an amount of from greater than 0% to about 0.7% based on the dry weight of the calcium sulfoaluminate cement. Preferably, the carboxylic acid/salt is present in an amount from about 0.1% to about 0.6% based on the dry weight of the calcium sulfoaluminate cement. When tartaric acid is the carboxylic acid, it is preferred that the tartaric acid be present in an amount from 0.17% to 0.5% based on the dry weight of the calcium sulfoaluminate cement.

The effectiveness of each specific carboxylic acid is different and is based upon its ability to chelate calcium. In the present invention, the following carboxylic acids are listed in the order of most effective to least effective: tartaric acid, citric acid, glutamic acid, glutaric acid, glycolic acid, formic acid, and gluconic acid. One skilled in the art would be able to determine the actual effective dose for each specific carboxylic acid.

The amount of phosphono alkyl carboxylic acid/salt is preferably kept low because of its low threshold value. The threshold value is the minimum amount needed

to be effective. Carboxylic acids/salts have a higher threshold value as compared to a phosphono alkyl carboxylic acid/salt. When carboxylic acids/salts are used alone at high levels, not only is the cement retarded, but also the compressive strength of a resulting cement is reduced. By using phosphono alkyl carboxylic acid/salt alone or in combination with a carboxylic acid/salt, the overall effective dose of the combination is lower than the effective dose of the carboxylic acid/salt alone, which results in retardation of the calcium sulfoaluminate cement without a significant reduction in the compressive strength of a resulting cement.

Further, when phosphono alkyl carboxylic acid/salt is used in combination with a carboxylic acid/salt, the retardation of the calcium sulfoaluminate cement is greater than the retardation when phosphono alkyl carboxylic acid/salt or the carboxylic acid/salt is used alone. Also, the combination provides a level of retardation beyond what would be expected of the combination, additively. Specifically, Figure 2 shows that the combination of the phosphono alkyl carboxylic acid/salt and the carboxylic acid/salt provides for a longer set time than when either is used alone.

In comparison, it has also been found that conventional chelators, such as hydroxyethylidenediphosphonic acid (HEDP) and ethylenediaminetetraacetic acid (EDTA) have no ability to retard the formation of ettringite in calcium sulfoaluminate cements.

The cementitious formulation of the present invention can further comprise other cements used in combination with the calcium sulfoaluminate cement. Examples of these other cements include, but are not limited to, portland, pozzolanic, and mixtures thereof. These other cements can replace up to about 70 to 80% of the calcium sulfoaluminate cement, without altering the effect of the retarder of the present invention.

The cementitious formulation of the present invention may further comprise aggregate. Examples of aggregate include, but are not limited to, silica, quartz, crushed round marble, glass spheres, granite, limestone, calcite, feldspar, alluvial sands, any other sands, any other durable aggregate, and mixtures thereof.

The cementitious formulation of the present invention may additionally comprise any cement additive that does not adversely affect the advantageous results obtained by the present invention. Examples of additives include, but are not limited to, dispersants, defoaming agents, air-entraining or air detraining agents, corrosion inhibitors, water reducing agents, pigments, and mixtures thereof.

The cementitious formulation of the present invention is activated upon the addition of water. The water to cement ratio (W/C) generally ranges from about 0.28 to about 0.5 based on the dry weight of all cements in the cementitious formulation.

Another embodiment of the present invention provides a method of retarding the set of a calcium sulfoaluminate cementitious formulation without substantially reducing achievable compressive strength. The method includes providing in the cementitious formulation, a retarder comprising at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid. The calcium sulfoaluminate cementitious formulation contains a calcium sulfoaluminate cement and may contain other cements, aggregates, and additives that do not adversely affect the advantageous results obtained by the present invention. Water is added to the calcium sulfoaluminate cementitious formulation to cause the formulation to set.

The preferred phosphono alkyl carboxylic acid is 2-phosphono-1,2,4-butane tricarboxylic acid.

The retarder in the method of the present invention may further comprise a second component that is at least one of a carboxylic acid and a salt of a carboxylic acid, as described above.

EXAMPLES

Example 1

A comparison of set retarders is performed. The set of a control mixture of calcium sulfoaluminate cement is compared to those of calcium sulfoaluminate cement mixtures containing tartaric acid at 0.5%, citric acid at 0.5%, and 2-phospono-1,2,4-

butane tricarboxylic acid (BAYHIBIT (trade mark) AM from Bayer Corporation, Pittsburgh, Pennsylvania) at 1% based on the dry weight of the calcium sulfoaluminate cement. The calcium sulfoaluminate cement used is sold under the trademark ULTIMAX from Ultimax Corp., Huntington Beach, California. The results of the comparison, determined by calorimetry, are shown in Figure 1. The units of measurement in Figure 1 are μg/calorie/second which is proportional to the heat of hydration of the samples.

As shown in Figure 1, it can be seen that all three acids reduce the intensity, but not the sharpness of the first major peak of the pure calcium sulfoaluminate cement. In theory, this peak indicates the heat release due to the setting of the cement. The second peak in the curve is more rounded and is believed to indicate an increase in strength development. In all cases, the acids reduce the intensity of this curve and significantly broaden the curve out. The tartaric acid and citric acid behave comparably, while the height for the PBTC curve is maintained over a greater time. It is believed that this is why PBTC has higher strength development for a given retardation.

Example 2

Mixtures of calcium sulfoaluminate cements are prepared with various combinations of the retarders of the present invention. The setting time and the 2 hour compressive strength are measured.

Cementitious Formulation	
Calcium Sulfoaluminate Cement (ULTIMAX)	1600 g (32%)
Dry Sand	3400 g (68%)
water	480 ml
water to cement ratio	0.3

Components added by weight percent of dry cement

Component A: 2-phospono-1,2,4-butane tricarboxylic acid

Component B: Tartaric Acid

The results of the above mixtures are listed below in Table 1.

Table 1

Mix Number	Component (wt.%) (A)	(B)	Setting Time (min)	2 Hour Compressive Strength (Mpa)
1	0.0	0.0	17	41.06
2	0.1	0.0	35	38.45
3	0.4	0.0	38	3.03
4	0.0	0.2	25	26.55
5	0.0	0.8	40	1.20
6	0.2	0.1	40	19.77
7	0.1	0.2	41	20.62

Example 3

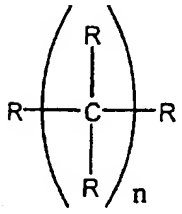
The dosages of PBTC, tartaric acid, and the combination of PBTC with tartaric acid are varied to determine the set time of a calcium sulfoaluminate cement. ULTIMAX cement is used. Also, the 2 hour compressive strength of the mixture with PBTC and the mixture with tartaric acid is measured. The results are shown in Figure 2.

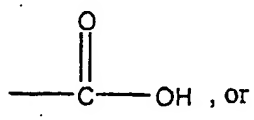
As is shown in Figure 2, as the dosage of retarder increases, the 2 hour compressive strength decreases showing that the mixture is retarded and not yet fully set.

It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

CLAIMS

1. A set retarding admixture for calcium sulfoaluminate cements comprising a first component that is at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid, and a second component that is at least one of a carboxylic acid and a salt of a carboxylic acid, and wherein the phosphono alkyl carboxylic acid has the general structure shown below:



wherein R is independently selected from -H, 

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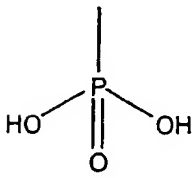


and n is an integer from 3 to 6, with the proviso that at least one R is $PO(OH)_2$.

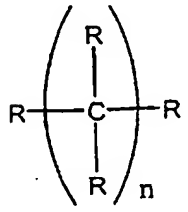
2. An admixture according to claim 1, wherein the phosphono alkyl carboxylic acid is 2-phosphono-1,2,4-butane tricarboxylic acid.

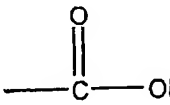
3. An admixture according to claim 1 or claim 2, wherein the salt of a phosphono alkyl carboxylic acid is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, ammonium, and mixtures thereof.

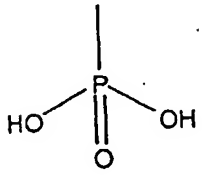
4. An admixture according to any one of claims 1-3, wherein the carboxylic acid is selected from the group consisting of tartaric acid, citric acid, glutamic acid, glutaric acid, glycolic acid, formic acid, gluconic acid, and mixtures thereof, and wherein the salt of a carboxylic acid is selected from the group consisting of a salt of tartaric acid, a salt of citric acid, a salt of glutamic acid, a salt of glutaric acid, a salt of glycolic acid, a salt of formic acid, a salt of gluconic acid, and mixtures thereof.

5. An admixture according to claim 4, wherein the salt of any of tartaric acid, citric acid, glutamic acid, glutaric acid, glycolic acid, formic acid, gluconic acid is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, ammonium, and mixtures thereof.

6. A cementitious formulation comprising a calcium sulfoaluminate cement and a retarder, wherein the retarder comprises a component being at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid, and wherein the phosphono alkyl carboxylic acid has the general structure shown below:



wherein R is independently selected from -H,  , or



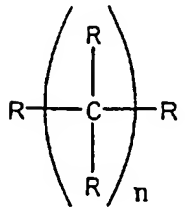
and n is an integer from 3 to 6, with the proviso that at least one R is $PO(OH)_2$.

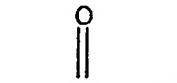
7. A cementitious formulation according to claim 6, wherein the component is present in an amount from greater than 0% to about 0.4% based on the dry weight of the calcium sulfoaluminate cement.

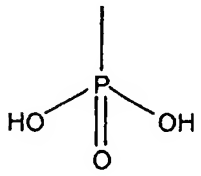
8. A cementitious formulation according to claim 7, wherein the salt of phosphono alkyl carboxylic acid is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, ammonium, and mixtures thereof.

9. A method of retarding the set of a calcium sulfoaluminate cementitious formulation without substantially reducing achievable compressive strength, comprising providing in said cementitious formulation, a retarder comprising a

component being at least one of a phosphono alkyl carboxylic acid and a salt of a phosphono alkyl carboxylic acid, and wherein the calcium sulfoaluminate cementitious formulation comprises a calcium sulfoaluminate cement, and wherein the phosphono alkyl carboxylic acid has the general structure shown below:



wherein R is independently selected from -H,  , or



and n is an integer from 3 to 6, with the proviso that at least one R is $PO(OH)_2$.

10. A method according to claim 9, wherein the retarder further comprises a second component that is at least one of a carboxylic acid and a salt of a carboxylic acid.

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Application No: GB 0004725.8 **Examiner:** Miss M Kelman
Claims searched: 1 to 10 **Date of search:** 12 May 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C1H HAR

Int Cl (Ed.7): C04B 24/04, 24/06, 28/06

Other: ONLINE: EPODOC, JAPIO, TXTE, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 2327417 A	ALBRIGHT & WILSON	
A	GB 2240334 A	SANDOZ	
A	US 5398759 A	HALLIBURTON	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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